Project Title: Effect of Surface Chemical Heterogeneity on Nanoparticle Adsorption at the Oil-Water Interface
PI: Claribel Acevedo-Vélez, University of Puerto Rico-Mayaguez

Progress of the research. The goal of the research conducted under this PRF DNI grant is to study the effect of changing the nature and composition of polar functional groups on the adsorption of chemically heterogeneous nanoparticles at the oil-water interface. An experimental approach based on the use of gold nanoparticles (AuNPs) functionalized with binary mixtures of alkanethiols displaying nonpolar (methyl, (CH_3)) and polar (hydroxyl (OH)), amine (NH_2), guanidine (Gdn)) groups as a model system was followed. The work conducted during the first year of the grant focused on: 1) preparation and characterization of chemically functionalized AuNPs; 2) interfacial tension measurements to study adsorption of functionalized AuNPs to oil-water interfaces; 3) development of a method based on image cytometry to measure size distributions of emulsion droplets as a function of time.

The first task consisted on preparing and characterizing AuNPs. Commercially available nanoparticles of 10 nm or 250 nm radius were incubated in ethanolic solutions containing binary mixtures of the alkanethiols described above to prepare chemically heterogeneous AuNPs. A molar composition of 40% polar/60% nonpolar groups was used for initial studies. AuNPs were characterized using FT-IR spectroscopy and X-ray photoelectron spectroscopy to confirm immobilization of alkanethiols and presence of functional groups on AuNP surfaces. NMR will be used next to confirm the ratio of polar to nonpolar groups on AuNP surfaces. Zeta potential measurements were conducted to assess AuNP surface charge under different pH conditions.

The energy of adsorption of nanoparticles to the oil-water interface depends on particle size, oil-water interfacial tension, and particle wettability to the oil or water phases (contact angle, θ). Initial oil-water interfacial tension (IFT) measurements revealed differences on the adsorption behavior of functionalized AuNPs (10 nm radius) to toluene/water and hexane/water interfaces (**Figure 1**). In the case of toluene, the IFT decreased only slightly upon adsorption of the nanoparticles to the interface (up to 4 mN/m), with the smallest change observed for the OH/CH_3 AuNPs. For hexane, a decrease in IFT of up to 10 mN/m was measured, with the largest change observed for the NH_2/CH_3 AuNPs. Similar trends were observed for nanoparticles of 250 nm radius.
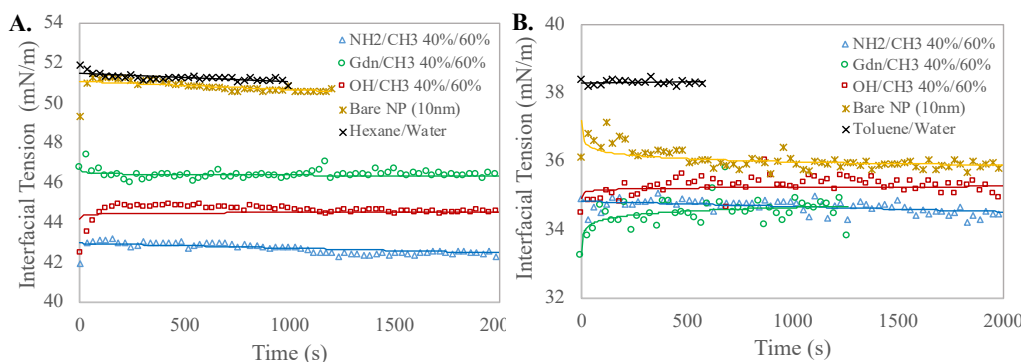

Figure 1. Dynamic interfacial tension for AuNPs functionalized with polar/nonpolar groups at 40%/60% molar composition for a (A) toluene or (B) hexane droplet in deionized water. Lines are added to guide the eye.

Figure 2. Toluene-in-water emulsions (2 vol% oil) observed as a function of time. Emulsions were prepared by homogenizing a mixture of oil and AuNP dispersions in deionized water (~0.001 vol% NPs) for 1 minute at 10,000 rpm.

Nanoparticle adsorption to the oil-water interface was also assessed by studying oil-in-water emulsions. Preliminary emulsion stability studies (**Figure 2**) further suggest that adsorption of the functionalized AuNPs to the oil-water interface depends in part on the nature of the polar groups displayed on their surface and may be a result of differences in particle wettability. Figure 2 shows that, over a period of four hours, toluene-in-water emulsions completely phase-separate for the NH_2/CH_3 and the Gdn/CH_3 AuNPs. However, creaming is observed for the OH/CH_3 AuNPs, showing a different mechanism for emulsion destabilization. It is important to note that toluene-water IFT was not significantly lowered by any of the AuNPs tested. Therefore, based on the observed emulsion destabilization mechanism, OH/CH_3 particles may have a more favorable wettability to remain adsorbed at the interface (e.g., contact angle at the toluene-water interface ~90º). Inspection of Figure 2 also reveals that the AuNPs are removed to the toluene phase. For Gdn/CH_3 and OH/CH_3, a nanoparticle dispersion (indicated by the red color) is observed on the upper oil layer. In contrast, NH_2/CH_3 AuNPs are removed as aggregated nanoparticles, indicated by the dark upper oil layer. This suggests that NH_2/CH_3 nanoparticle aggregation may be influencing adsorption to the oil-water interface. Stability studies were also conducted for hexane-in-water emulsions (data not shown). Phase-separation was observed for all the AuNP chemistries tested within one hour of emulsion preparation. Although data in Figure 1 suggests that these particles can adsorb to the hexane-water interface to
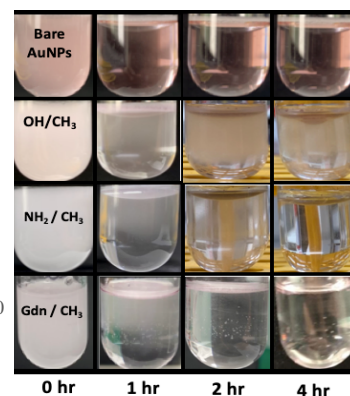
lower the IFT, this change was not sufficient for the particles to remain adsorbed at the interface to stabilize emulsions. Therefore, these results further suggest that particle wettability or affinity to either the water or oil phase plays a significant role on nanoparticle adsorption at the oil-water interface for the surface chemistries tested.

Finally, a method based on the use of image cytometry to measure size distributions of oil droplets dispersed in aqueous solutions as a function of time was developed. This method allows for characterization of size distribution of many drops (thousands) in very short periods of time (minutes), thus allowing analysis of a larger number of samples in one experiment and providing an advantage over the use of optical microscopy for emulsion droplet size characterization. **Figure 3** shows preliminary measurements demonstrating the feasibility of using image cytometry to characterize emulsions. Changes on the size distributions of hexane droplets dispersed in an aqueous phase were measured immediately after emulsion preparation, and then every 15 minutes, for a total of 60 minutes. Droplet size is shown to decrease over time due to smaller droplets (previously not detected by the image cytometer) coalescing and creating larger droplets before separating from the emulsion. In general, increasing the pH of the aqueous phase to 10.5 (when all tested AuNPs have a negative surface charge as determined through zeta potential measurements) resulted in emulsions with smaller droplet sizes as compared to pH 4 (when NH_2 and Gdn groups are protonated). However, at pH 4, smaller droplet sizes were measured for the NH_2/CH_3 AuNPs as compared to other chemistries, suggesting a difference on nanoparticle adsorption to the oil-water interface during the emulsification process. After 48 hours of emulsion preparation, samples at pH 4 showed complete phase separation, while samples at pH 10.5 showed emulsion destabilization by creaming (data not shown). Overall, results from these preliminary experiments show that image cytometry is a useful tool to characterize emulsion size distributions as a function of time under different experimental conditions.

Figure 3. Size distributions as a function of time for hexane-in-water emulsions with aqueous phase at (A) pH 4 and (B) pH 10.5, obtained using image cytometry.

Based on developed experimental methods and preliminary results obtained during the past year, future studies will be focused as follows. Functional group composition (polar-to-nonpolar group ratio) on AuNP surfaces will be changed to tune particle wettability. Contact angles of oil and water droplets will be measured on planar surfaces functionalized with these binary mixtures of alkanethiols to assess surface wettability. In addition, nanoparticle size and concentration, pH, and oil/water ratio will be changed as these variables can also affect particle adsorption to the oil-water interface and emulsion properties. IFT measurements will be conducted as a function of pH to study the effect of the charge state of the ionizable polar groups (Gdn and NH_2) on nanoparticle adsorption at the oil-water interface. Finally, nanoparticle aggregation in bulk aqueous solution will be studied to determine its influence on oil-water interfacial behavior and emulsion properties.

Impact of the research on the career of the PI. The PRF DNI grant has been fundamental for initiating the PI's career, as this was the first grant received by her as an independent researcher. The funds allowed the PI to recruit the first graduate student in her lab, which led to establishing a new line of research in the lab, developing new experimental protocols, and applying the concepts and techniques learned to other projects. Therefore, this grant has allowed the PI to establish and grow her research program.

Impact of the research on the career of participating students. The PRF DNI grant has supported a graduate student in the Department of Chemical Engineering. This student was initially supported as an undergraduate in the PI's laboratory, and his interest in the project motivated him to apply for the Chemical Engineering graduate program. While conducting this research, the student has been trained in laboratory safety, design and execution of experiments and data analysis, and continues to improve his ability to work independently in the project. Moreover, he has mentored two undergraduate students working in the project and has presented this PRF funded research at local (2018 Forward Summit, Puerto Rico Science, Technology and Research Trust) and national (2019 ACS Spring National Meeting) conferences. Therefore, this grant has allowed the student to acquire skills that will be fundamental in his career upon completion of his MS degree. In addition, two undergraduate students have worked on the project and have been trained on laboratory safety, experimental work and data analysis. For one of the undergraduate students, this was his first research experience and motivated him to apply for and participate in a summer research experience for undergraduates at the University of Wisconsin-Madison, and now plans to co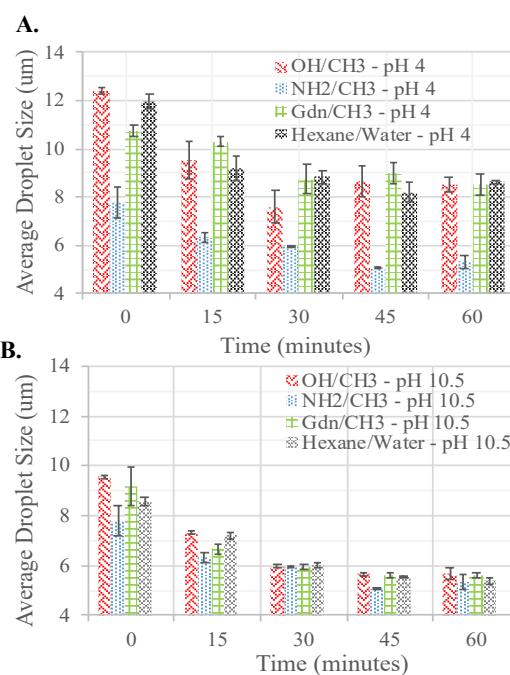ntinue doctoral studies upon graduation.